REVIEW ARTICLE

Pt–C interactions in carbon-supported Pt-based electrocatalysts

Yu-Xuan Xiao[1], Jie Ying (✉)[1], Hong-Wei Liu[1], Xiao-Yu Yang (✉)[2]

1 School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China
2 State Key Laboratory of Advanced Technology for Materials Synthesis and Processing & Shenzhen Research Institute & Joint Laboratory for Marine Advanced Materials in Pilot National Laboratory for Marine Science and Technology (Qingdao),
Wuhan University of Technology, Wuhan 430070, China

Abstract Carbon-supported Pt-based materials are highly promising electrocatalysts. The carbon support plays an important role in the Pt-based catalysts by remarkably influencing the growth, particle size, morphology, dispersion, electronic structure, physiochemical property and function of Pt. This review summarizes recent progress made in the development of carbon-supported Pt-based catalysts, with special emphasis being given to how activity and stability enhancements are related to Pt–C interactions in various carbon supports, including porous carbon, heteroatom doped carbon, carbon-based binary support, and their corresponding electrocatalytic applications. Finally, the current challenges and future prospects in the development of carbon-supported Pt-based catalysts are discussed.

Keywords Pt–C interactions, Pt-based materials, carbon support, electrocatalysis

1 Introduction

Pt-based nanostructures are the most popular and universally available electrocatalysts owing to the special 5d orbital structure of Pt, which makes it highly active [1–12]. However, nanosized Pt is vulnerable to aggregation, oxidation, dissolution and Ostwald ripening, resulting in a decrease of activity and stability of Pt catalysts. Owing to its large specific surface area that favors dispersion of active components, high electric conductivity, porous structures and low cost, nanostructured carbon is the most important support for metal catalysts [13–16]. It is well-known that carbon supports

E-mails: yingj5@mail.sysu.edu.cn (Ying J.), xyyang@whut.edu.cn (Yang X.-Y.)

are not simply inert materials. Owing to the inherently higher electronegativity of C (2.55) compared to Pt (2.28), generally electrons are transferred from Pt to carbon, which will alter the electronic structures and physicochemical properties of both Pt and the carbon support [17–19]. Meanwhile, due to the electron transfer from Pt to carbon, the surface electron deficient Pt atoms will be less vulnerable to oxidation or dissolution, thus altering Galvanic potentials of Pt atoms. Such electron transfer will also lower the Fermi level of Pt 5d electrons, leading to a closer d band center to the Fermi level, which makes Pt more active toward the adsorption of adsorbates according to d band theory [20,21]. The benefits of altered electron densities, Galvanic potentials and Fermi levels of metals will enhance electron transfer at the electrode–electrolyte interface and thus accelerate electrode processes [22–24]. As a consequence, deposition of Pt on nanostructured carbon can improve its catalytic activity and stability.

Owing to their highly porous structure with large specific surface area, good electric conductivity and low cost, carbon black has been regarded as the best choice for the support of Pt electrocatalysts [22]. Different carbon black materials have been developed as supports for Pt catalysts, such as Vulcan XC 72, Black Pearls 2000, Ketjen EC300J and Denka black. Commercial Pt/C is a typical catalyst composed by 2–5 nm Pt nanoparticles supported on carbon black. The large specific surface area of carbon black facilitates the homogeneous dispersion of Pt nanoparticles on carbon surface, and the high dispersion and small particle size features guarantee the high performance of Pt catalyst. Moreover, the porous feature of carbon black will favor the adsorption of active components in catalytic reactions, the high electric conductivity of carbon black is critical for electrochemical process, and the low cost of carbon black promotes the commercialization of Pt/C catalyst, all of which render

the broad utilization of commercialized Pt/C in catalysis and a benchmark catalyst for Pt-based materials [25].

In studies of carbon-supported Pt-based electrocatalysts, more and more attention has been paid to the effects of Pt–C interactions [26–30]. By using different carbon supports, different Pt–C interactions will take place in electrocatalysts, which will affect both its properties and functions. Thus, the strong Pt–C interactions are generally beneficial for enhancement of the properties and stabilities of the electrocatalysts [31–37]. Therefore, an understanding of Pt–C interactions will greatly facilitate the design and synthesis of high-performance carbon-supported Pt-based electrocatalysts.

Because the field of carbon-supported Pt-based electrocatalysts has advanced very rapidly in recent years, few reviews have focused on studies of Pt–C interactions. Thus, an overview of the recent progress made in developing carbon supported Pt-based electrocatalysts is highly desired. Figure 1 shows the diagram outlining the different Pt–C interactions brought about by different carbon supports. This review focuses mainly on Pt–C interactions in Pt-based catalysts that occur in the presence of different carbon materials including the porous carbon supports (ordered mesoporous carbon, metal–organic frameworks (MOFs)-derived porous carbon and three-dimensional (3D) porous carbon, Section 2), heteroatom doped carbon supports (nitrogen-, boron-, sulfur- and multiple doped carbon, Section 3), carbon-based binary supports (carbon/carbon, carbon/oxides and carbon/organics, Section 4), and the applications of these materials in electrocatalysis (Section 5). Great attention is given to the effects of Pt–C interactions on activity/stability of Pt-based catalysts. The review ends by discussing the current challenges and future prospects in the design of high-performance carbon-supported Pt-based catalysts (Section 6).

2 Porous carbon supports

Porous carbon materials have the meritorious features of high specific surface areas, large pore volumes, tunable porous structures, controllable macroscopic morphologies, and well-tailored pore dimensions, which all have significant relevance to the design and synthesis of porous carbon materials [38–41]. As supports, the porous carbon materials have (1) high surface areas to promote deposition or nucleation of Pt nanocrystals on their surfaces, (2) well-defined pores that serve as confined regions for the growth of Pt nanoparticles to facilitate formation of small particle sizes and limit aggregation, and (3) highly porous structures that facilitate mass transport during electrochemical reactions. As a result, many methods, such as hard template, soft template and direct pyrolysis, have been developed to synthesize various porous carbon materials with different porous size and to investigate their characteristics as supports for Pt electrocatalysts. Some typical examples are listed in Table 1.

2.1 OMC

OMC is a popular support because it has well-controlled porosities, which makes it suitable for growth or deposition of nanosized Pt. Template methods are usually employed to synthesize OMC. During the synthetic procedure, templates having well-defined structures are combined with a carbon source [67–70]. High temperature carbonization and removal of the templates by chemical etching give rise to carbon materials that replicate the structure of the template, and thus have ordered mesoporous structure. By adjusting the nature of the template, ordered macro- or micro-porous carbon materials can be obtained [71]. The discussion below focuses on OMCs as typical hierarchical porous carbon supports for Pt-based catalyst. Figure 2 shows some typical examples of OMC supported Pt catalysts.

In one effort, Wan et al. [72] fabricated $SiO_2@SiO_2$/resorcinol formaldehyde nanospheres as a template for OMC generation. Upon carbonization, the resorcinol formaldehyde template is removed to form hollow mesoporous carbon spheres, which are used as a support for sub-nanometer Pt clusters. The formed highly active Pt clusters are highly stabilized by the carbon support (Fig. 2(a)). In this general approach, different carbon sources can be used to create other types of OMCs. For example, Kuang et al. [73] utilized polydopamine as a carbon source along with SiO_2 as the template to prepare
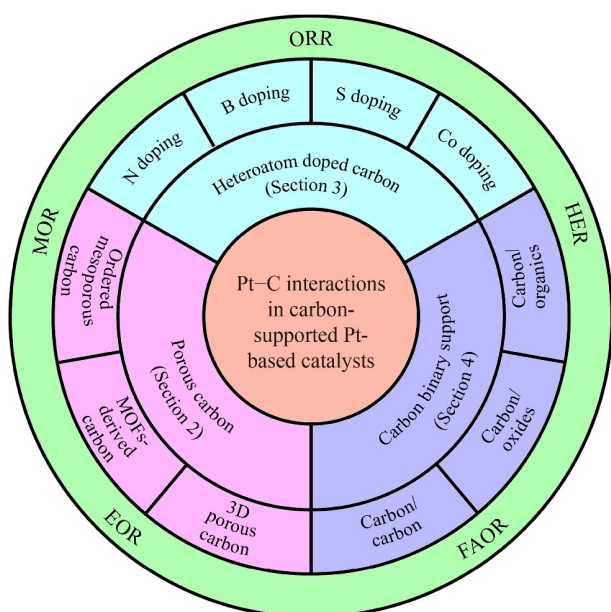

Fig. 1 Diagram outlining the different Pt–C interactions brought about by different carbon supports.

Table 1   A summary of the pore size of carbon materials synthesized by different methods

Carbon material	Synthetic method	Pore type	Mean pore size	Ref.
Zeolite-templated carbon	Hard template	Micropore	1.2 nm	[42]
3D graphene-like microporous carbon	Hard template	Micropore	1.33 or 1.21 nm	[43]
Microporous 3D graphene-like carbon	Hard template	Micropore	<1.3 nm (74%) 1.3–2.2 nm (8%)	[44]
Disordered amorphous microporous carbon	Hard template	Micropore	1.1–3.0 nm	[45]
Microporous carbon nanospheres	Soft template	Micropore	0.4–2 nm	[46]
Hierarchically porous amorphous carbon	Direct pyrolysis	Micropore	0.4–1.08 nm	[47]
Disordered amorphous ultramicroporous carbon	Direct pyrolysis	Micropore	0.6–0.76 nm	[48]
Amorphous microporous carbon	Hydrothermal/direct pyrolysis	Micropore	0.7–3 nm	[49]
Mesoporous carbon hollow spheres	Hard template	Mesopore	13.9 nm	[50]
Ordered mesoporous carbons (OMCs)	Hard template	Mesopore	3.0–5.0 nm	[51]
Porous carbons	Soft template	Mesopore	5.1 nm	[52]
OMCs	Soft template	Mesopore	4.5 nm	[53]
OMCs spheres	Soft template	Mesopore	5 nm	[54]
Mesoporous carbon nanospheres	Soft template	Mesopore	5–37 nm	[55]
Mesoporous carbon	Direct pyrolysis	Mesopore	11 nm	[56]
Porous carbon microspheres	Hydrothermal	Mesopore	18.4–26.1 nm	[57]
3D ordered macroporous carbon nanocomposite	Hard template	Mesopore/macropore	1–100 nm	[58]
Ordered macroporous carbon	Hard template	Macropore	~255 nm	[59]
3D ultrathin macroporous carbon	Hard template	Macropore	~300 nm	[60]
Macroporous carbon rods	Soft template	Macropore	~100 nm	[61]
3D hierarchical bimodal macroporous carbon nanospheres	Soft template	Macropore	~120 nm	[62]
Cornstalk-derived macroporous carbon	Direct pyrolysis	Macropore	5.0–20.0 μm	[63]
Macroporous carbon	Direct pyrolysis	Macropore	250 nm	[64]
Eggplant-derived macroporous carbon tubes	Direct pyrolysis	Macropore	40–50 μm	[65]
Well-ordered macroporous carbon	Direct pyrolysis	Macropore	4–40 μm	[66]

N-doped hollow carbon spheres (Fig. 2(b)). The carbon support formed in this manner has a highly interconnected 3D porous structure with a high specific surface area, which can embed Pt single atoms to prevent them from aggregation. Moreover, the carbon support can form a strong metal-support interaction with Pt, which significantly tailors the electronic structure of Pt 5d states that promotes reduction of adsorbed proton, facilitates H–H coupling, both of which cause a higher electrocatalytic activity for the hydrogen evolution reaction (HER).

Our group has also developed a series of OMCs possessing different kinds of pore channels and used them to confine Pt nanoparticles. By applying mesocellularalumino silicate foam as a template, a continuous 3D porous structure was obtained [74]. Use of this carbon material as the support enabled fabrication of a unique one particle@one cell structure (Fig. 2(c)), which effectively prevents the occurrence of aggregation during the growth of PtPd nanoparticles that have significantly enhanced durability as a catalyst [75]. Furthermore, by utilizing SBA-15 as template, an OMC with straight pore channels was synthesized. To deposit metal nanoparticles inside the pores of this OMC, a high viscosity strategy was developed to ensure that PtPd nanocrystals in the OMC have small size and high dispersity (Fig. 2(d)), resulting in the both high electrocatalytic activity and stability.

2.2   MOFs-derived porous carbon

As a novel type of crystalline porous material with highly ordered permanent pore structures and diverse compositions, MOFs have been used as precursors for the construction of porous carbon materials [76]. By employing pyrolysis at high temperatures under an inert atmosphere, Liu et al. [77] fabricated a porous carbon material. The material generated in this way has several advantageous features, including (1) inherited merits of MOFs including high specific surface area, ordered pore structure and adjustable pore size, (2) controlled sizes and morphologies of the produced porous carbon material by using different MOFs materials, and (3) the capability of doping of highly dispersed heteroatoms arising from the ligands in the MOFs. As a result, MOFs-derived porous carbon materials can serve as designed and versatile supports for Pt-based electrocatalysts. Figure 3 shows some typical examples of MOFs-derived porous carbon supported Pt catalysts.

By using zeolitic imidazolate framework (ZIF)-67 as the precursor, Zhang et al. [78] prepared a quasi-Pt-allotrope catalyst composed of hollow Pt_3Co@single-atom Pt on nitrogen-doped carbon (NC, Fig. 3(a)). This unique nanoarchitecture enables the inner and exterior spaces to be easily accessible thus giving an extra-high active surface area and active sites for the penetration of both aqueous and organic electrolytes. Also, the doped N atoms greatly modify the electronic structure, and the carbon shell provides protection for the inner Pt_3Co nanoparticles from agglomeration, endowing the catalyst with high electrocatalytic activity and stability. Wu et al. [79] used the commercially available Cu-MOF as a
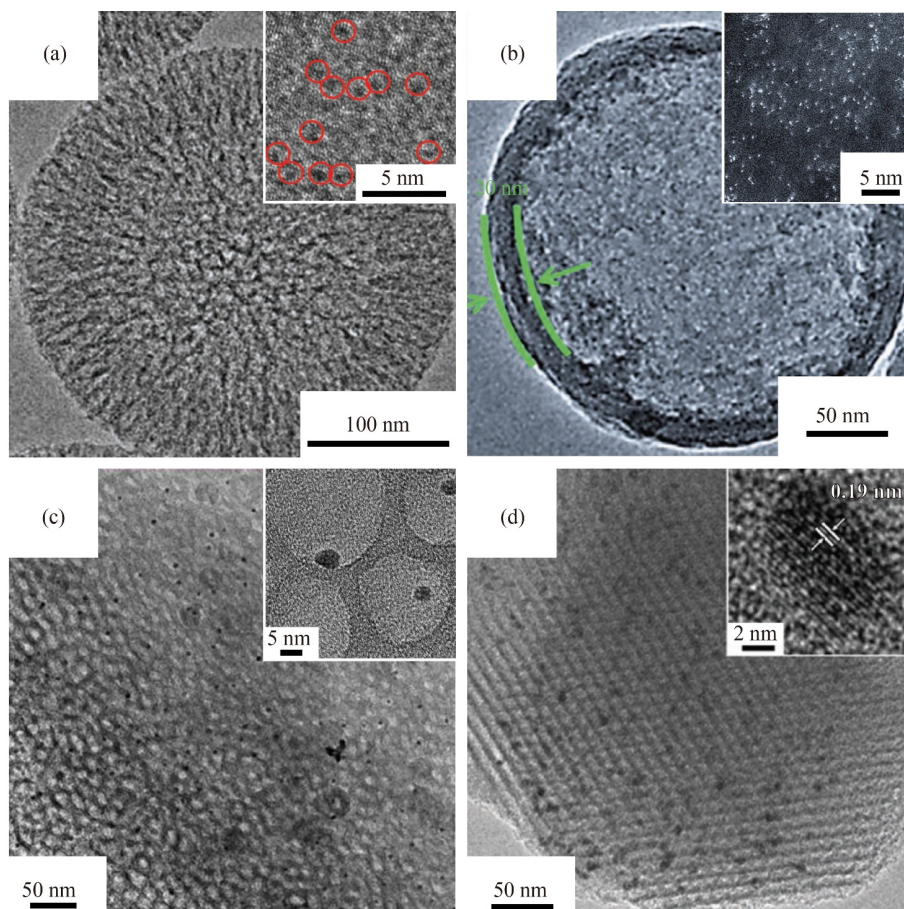
Fig. 2 Pt-based nanoparticles supported in OMC with (a) hierarchically hollow straight mesopores in thick wall, (b) hierarchically hollow straight mesopores in thin wall, (c) interacted mesopores, and (d) straight mesopores. Reprinted with permission from Ref. [72], copyright 2020, Wiley-VCH, Ref. [73], copyright 2021, Wiley-VCH, Ref. [74], copyright 2014, Elsevier, and Ref. [75], copyright 2016, Royal Society of Chemistry.

precursor to synthesize a porous carbon support for highly dispersed Pt nanoparticles and amorphous nickel. The carbon support produced in this manner has hierarchically porous features, in which the micropores provide a high surface area for deposition sites to disperse Pt, and the mesopores across the microporous matrix provide accessibility to reactant molecule for quick diffusion (Fig. 3(b)), resulting in a high performance in the methanol electrochemical oxidation reaction.

Our group has also investigated MOF-derived porous carbons for Pt supports. ZIF-8 nanoparticles were utilized to embed Pt nanoparticles, and carbonization gave rise to highly dispersed Pt nanoparticles embedded in the hierarchically hollow porous carbon polyhedron (Fig. 3(c)) [80]. Nitrogen-doping, large surface area, hollow nanostructure and hierarchical pore system of the ZIF-8-derived carbon support play key roles giving this Pt-based electrocatalyst high performance toward the HER. Moreover, by using cobalt-based ZIF-67 as precursor, PtCo bimetallic nanoparticles are formed inside of the hierarchically porous carbon network to endow the electrocatalyst with both high activity and stability toward the oxygen reduction reaction (ORR, Fig. 3(d)) [81].

2.3 3D porous carbon

Different from the ordered mesoporous structure of OMC or the inherited microporous and/or mesoporous features of MOFs-derived porous carbon materials mentioned above, 3D porous carbon usually has 3D interconnected macroporous channels. Despite a larger pore size, 3D porous carbon has a 3D interconnected shape of channels, which may be quite irregular with a wide pore size distribution, far from the regular pore shape of OMC or MOFs-derived porous carbon materials. As a result, the specific surface area of 3D porous carbon is much smaller than that of OMC or MOFs-derived porous carbon materials. Even so, benefiting from its 3D macroporous architecture, 3D porous carbon possesses many extraordinary physical and chemical properties, which are unachievable in other types of carbon material, such as high strength, good thermal stability and high corrosion and oxidation resistance [82]. Applied in catalysis, the interconnected macroporous channels will allow the transport of macromolecular reactants, which will ensure the high kinetics of catalytic process. Figure 4 shows some typical examples of 3D porous carbon supported Pt
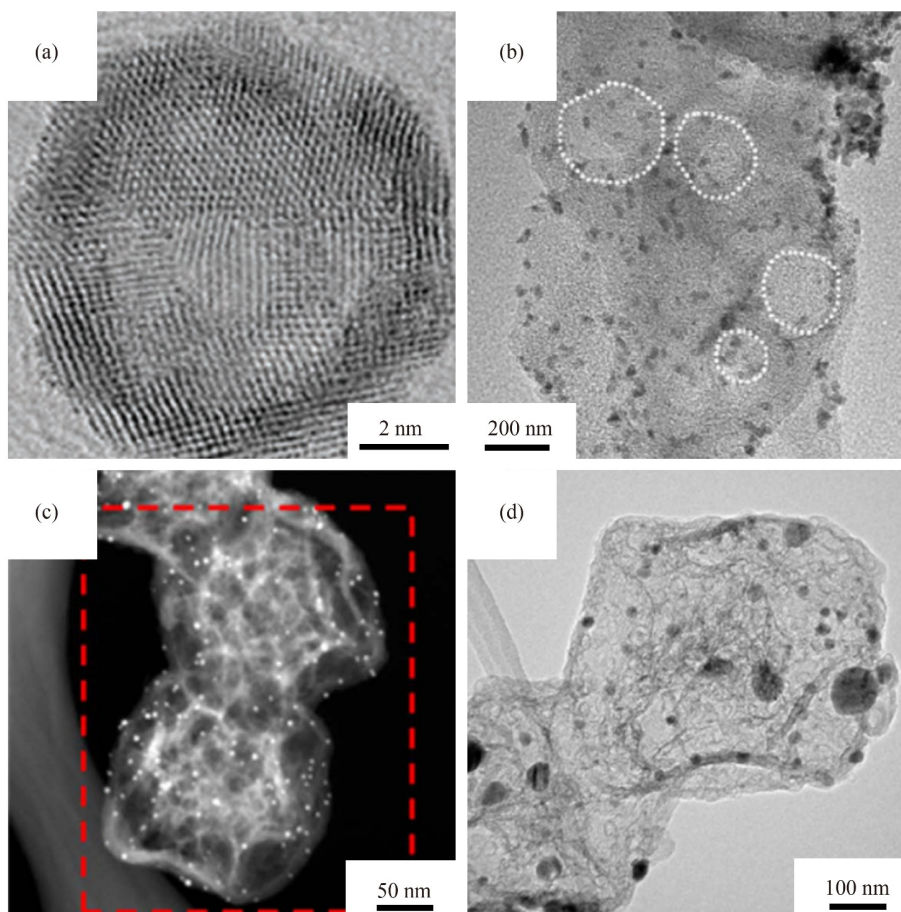
Fig. 3 Pt-based nanoparticles supported in/on MOFs-derived porous carbon. (a) Hollow PtCo and Pt single atoms encapsulated in MOFs-derived carbon shells. Reprinted with permission from Ref. [78], copyright 2018, American Chemical Society. (b) Pt nanoparticles supported on MOFs-derived porous carbon. Reprinted with permission from Ref. [79], copyright 2018, American Chemical Society. (c) Pt nanoparticles embedded in MOFs-derived hierarchically hollow porous carbon. Reprinted with permission from Ref. [80], copyright 2017, Elsevier. (d) PtCo and Co nanoparticles embedded in MOFs-derived hierarchically hollow porous carbon. Reprinted with permission from Ref. [81], copyright 2018, Elsevier.

catalysts. For example, Zhang et al. [83] produced vertically aligned carbon nanotube (CNT) arrays by using the chemical vapor deposition method involving pyrolysis of iron(II) phthalocyanine (Fig. 4(a)). In addition, Chen et al. [84] prepared CNT aerogels by mixing CNTs with organic carbon sources followed by pyrolysis (Fig. 4(b)). Both methods generated advanced CNT-based carbon materials with porous, interconnected and uniformly distributed 3D framework structures composed of CNTs, which highly facilitate mass transport and greatly enhance the performance of Pt materials. Ye et al. [85] synthesized a novel 3D carbon foam material by heat treatment of melamine resin sponge (Fig. 4(c)). This carbon foam support, which possesses a hierarchically porous structure that facilitates diffusion and adsorption of reactant molecules, can be used to generate high performance Pt electrocatalyst. Atwa et al. [86] synthesized nanoporous carbon films employing a similar replication method and silica templates, described in Section 2.1, that further assembled into OMC to films. The carbon material formed in this manner has a self-supported nanoporous

carbon scaffold structure (Fig. 4(d)). The high density of surface defects of the as-synthesized carbon films promotes uniform Pt nucleation with minimal agglomeration, and, and as a result, it can be used to create a high-performance Pt-based electrocatalyst.

3 Heteroatom doped carbon support

It is widely known that appropriate heteroatom doping leads to higher performance of electrocatalysts. However, the activities of the carbon supported Pt-based catalysts can be enhanced to greater extents by heteroatom doping because it also modifies the electronic properties of the carbon support to give it metallic behavior, in addition to modifying the nucleation and growth kinetics of Pt, providing anchoring sites for Pt nanoparticle deposition and introducing active sites for electrocatalytic reactions [87]. Extensive researches have been performed using heteroatoms with different properties, such as nitrogen,
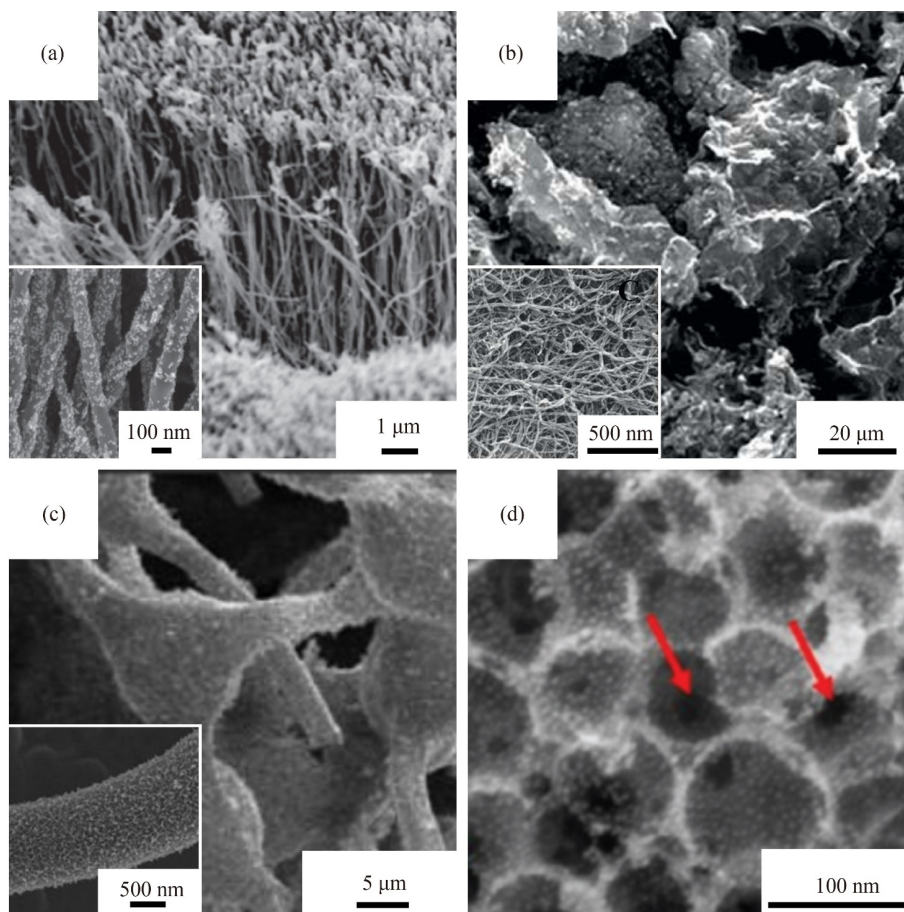
Fig. 4 Pt-based nanoparticles supported on 3D porous carbon of (a) CNT arrays, (b) CNT aerogels, (c) 3D carbon foam, and (d) OMC films. Reprinted with permission from Ref. [83], copyright 2011, Wiley-VCH, Ref. [84], copyright 2016, American Chemical Society, Ref. [85], copyright 2020, Elsevier, and Ref. [86], copyright 2021, Royal Society of Chemistry.

sulfur, phosphorous and boron. Two methods are commonly used to carry out heteroatom doping on carbon include *in situ* doping using precursors containing both C and heteroatoms, and post doping involving post-treatment of carbon with heteroatom-containing substances. Both methods enable greatly advanced design of physiochemical and electronic structures.

3.1 NC

Among various doping atoms, nitrogen is currently the most popular one because it beneficially changes both the electronic and structural properties of the carbon supports. Nitrogen has a larger electronegativity (3.04) than C (2.55), which will result in the electron transfer from carbon to nitrogen and thus improve the performance of the catalysts [88]. Owing to this beneficial feature, NC itself can serve as a superior electrocatalyst [89–91]. When the NC is used as the support for Pt, strong interaction between Pt and NC can be formed and bring following advantages: (1) the introduction of nitrogen atoms providing carbon atoms with a polar nature and hydrophilicity; (2) the functionalities and defects increase

the number of anchoring sites; (3) the electronic features of NC may improve the nucleation of Pt by changing the p-electron delocalization and influence the strength of interaction between Pt NPs and NC [92].

Direct high temperature treatment of MOFs causes transformation of the organic ligands to carbon, while retaining N species derived from ligands such as imidazole, pyridine, pyrrole amines will still maintain, forming NC support. Figure 5 shows a typical example of NC supported Pt catalysts. Zhang et al. [78] synthesized an NC material containing rich defects by using carbonization of a pyridine-based Co-MOF and amide (Figs. 5(a–d)). As a support for PtCo, the N8V4 vacancies (where N8 represents the number of nitrogen atoms and V4 indicates the number of vacant carbon atoms) within the carbon shell of the produced N-doped material coordinate with PtCo atoms, creating an asymmetrical electron distribution around the Pt/Co metal centers on the NC surface (Fig. 5(e)). Our group also developed an *in situ* method for synthesizing hierarchical porous N-doped carbon nanofibers (CNF) involving electrospinning and carbonization of both imidazole-based ZIF-8 nanoparticles and polyacrylonitrile as the carbon skeleton [93]. In the
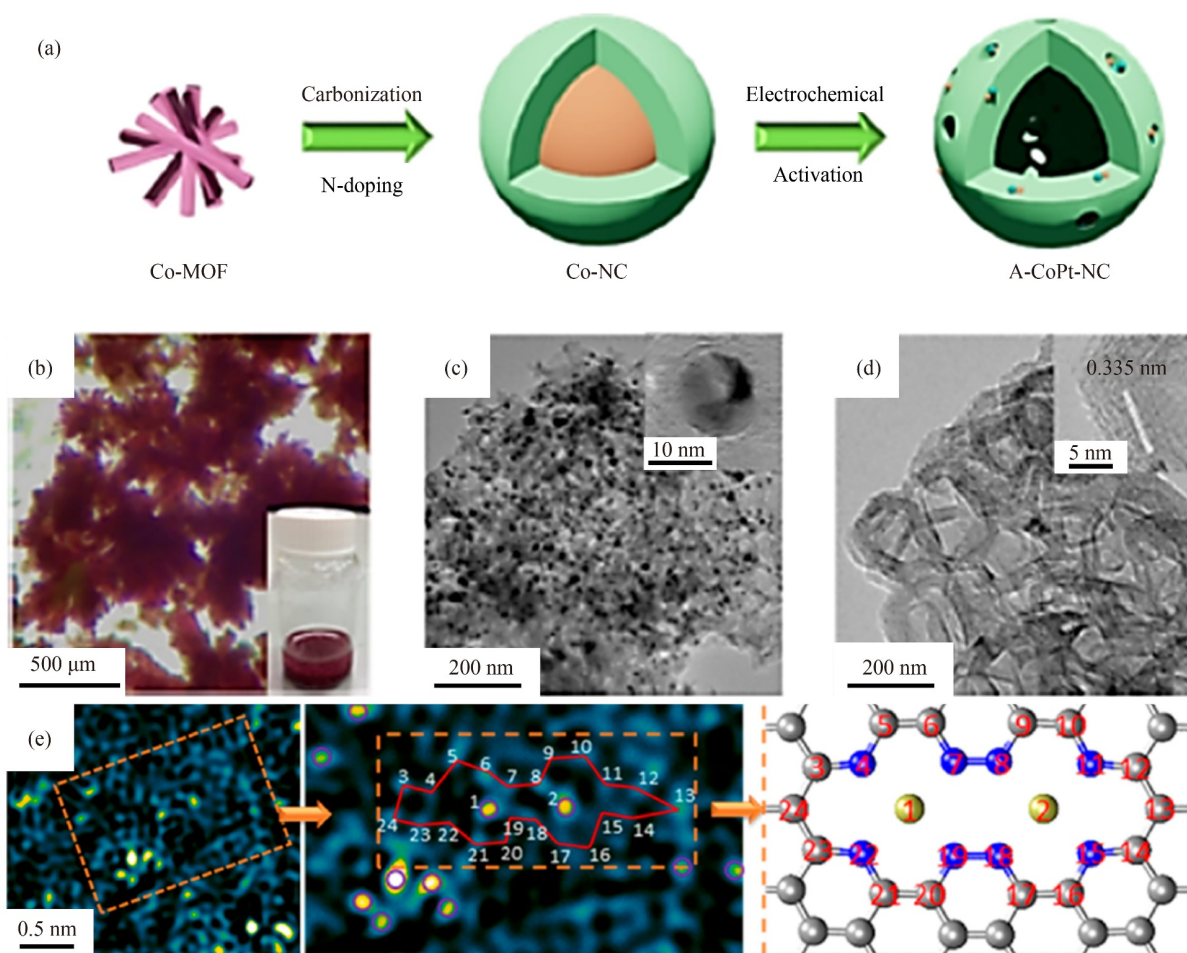
Fig. 5 (a) Illustration of the pathway for direct N doping of a carbon support derived from MOFs. (b–d) Morphology characterization of the samples. (e) Illustration of the defects and vacancies. Reprinted with permission from Ref. [78], copyright 2018, American Chemical Society.

carbon material with embed ultrafine Pt nanoparticles, the pyridinic N species in the NC strongly interacts with Pt to greatly enhance the heavy d−π effect and facilitate electron transfer from Pt and C to N atoms. These effects improve the electronic conductivity and hydrogen absorption behavior of the Pt nanoparticle-based electrocatalyst.

In addition to MOFs, other NC sources have been employed to create NC materials. For example, Bulushev et al. [94] synthesized N-doped mesoporous CNF by carbonizing a mixture of ethylene and ammonia. As supports for Pt single atoms, a pair of pyridinic nitrogen atoms at the edge of carbon support form a chelate with Pt atoms, providing an ionic/electron-deficient state that resists aggregation and has excellent stability under the reaction conditions. Luo et al. [95] developed a one-step solvothermal carbonization method using chitosan to prepare NC dots. As support for atomic Pt, this NC material maximizes the atomic efficiency of Pt and improves the charge transfer capability.

Post doping is a reliable strategy to form high-performance supports for Pt electrocatalysts. Different from *in situ* doping that incorporates N atoms during

formation of the carbon structure, post doping introduces N atoms onto the carbon surface, which might bring about different behaviors of the carbon supports. Ammonolysis is the most common strategy used for post N-doping of carbon. The process usually involves initial treatment of carbon material with HCl to remove impurities, and then reaction with HNO_3 to oxidize the carbon surface and final treatment with ammonia gas at high temperature. For example, Schmies et al. [96] generated N-doped commercial Vulcan XC 72R carbon black using the ammonolysis method. They found that during the ammonia gas treatment step, pyrrolic-N are the most abundant surface species at lower temperatures while pyridinic-N prevail at elevated temperatures. The Pt-based catalyst using NC synthesized at high temperature as the support possesses higher corrosion resistance and superior electrocatalytic performance. Hornberger et al. [97] have made the similar finding that the fraction of pyridinic-N increases with increased ammonolysis temperature while the fraction of pyrrolic-N decreases. As a support for Pt nanoparticles, the pyridinic-N dominated NC provides large numbers of active sites and

defects, which lead to enhancement of anti-corrosion properties and stability.

3.2 Boron-doped carbon (BC)

In contrast to nitrogen, boron has a lower electronegativity (2.04) than carbon. Therefore, in a BC system, boron atoms donate electrons to carbon. There are two kinds of B doping configuration into carbon: (1) in-plane doping, in which B atoms are sp^2-hybridized in the carbon lattice, will seldom alter the lattice parameters of carbon owing to the similar bond length of B–C bond (~1.50 Å) and C–C bond (1.42 Å); (2) vacant sites doping, in which B atom forms a BC_4 unit with C atoms, will torture the lattice of carbon. From the perspective of electronic interactions, in comparison with NC, BC has distinctive effects on carbon supports used in Pt-based catalysts. On the other hand, the formation energy of BC (~5.6 eV·atom^{-1}) is lower than that of NC (8.0 eV·atom^{-1}). Thus, the synthesis of BC as a support for Pt usually does not require high temperatures so that a liquid reaction system can be used to incorporate B into carbon [98]. The low electronegativity of B promotes redistribution of electron density toward carbon, leading to creation of more active electrons and a higher binding ability for reactants [99,100]. Moreover, with one less valence electron to the neighboring C, B-doping will induce a charge polarization in the carbon matrix, which is favorable for electrocatalysis.

Hu et al. [101] synthesized Pt/B-doped graphene catalysts by using a one-pot hydrothermal method with homemade graphene oxide as the substrate, $Pt(NH_3)_4(NO_3)_2$ as the Pt precursors and boric acid as the B source. In the process, B atoms are embedded into the graphene matrix, which enhances the Pt nucleation rate, promotes formation of more metallic Pt, and facilitates higher dispersion and smaller sizes of the Pt nanoparticles. Also, B in this support promotes electron donation to Pt and increases chemisorption of intermediates in the electrocatalytic reaction. Yao et al. [102] developed a two-step method for the post B-doping of carbon black. In the solvothermal system employed, $NiCl_2$ is first reduced by the organic solvent to generate Ni supported on the surface of carbon black. Then, the formed Ni atoms serve as catalysts for reduction of sodium borohydride to form B atoms on the carbon black. When used as the support for Pt catalyst, the B-doped carbon support plays an important role in controlling the size, dispersion as well as the adsorption/dissociation ability of Pt nanoparticles.

3.3 Sulfur-doped carbon (SC)

Unlike previously discussed effects created by N or B doping, negligible polarization (or charge transfer) exists in the C–S bond because of the similar electronegativities of S (2.58) and C. However, S atom substitution for C leads to SC that has a high charge and spin density, elevated band level and enhanced metallic properties [98]. Compared to N-doping, S-doping is more difficult to execute because of the atomic size of S and its different binding behavior [103]. Specifically, compared to N (65 pm) and B (85 pm), S (100 pm) has a larger radius than C (70 pm) that makes its substitution into sp^2 lattice difficult because it causes distortion of the planar C structure. Another difficulty is that S atoms in SC may poison Pt by inhibiting the active sites of Pt [104]. However, the strong interaction between Pt and SC can be utilized in the design of a stable Pt–S–C electrocatalysts [105]. Owing to the strong adsorption feature of S, the doped S atoms in carbon can serve as the anchoring sites for Pt nanoparticles, which highly facilitates the dispersity of Pt nanoparticles on the carbon surface, preventing them from further growth and aggregation [106]. For electrocatalysis, the electrochemical surface area is high relevant to the size and dispersity of Pt nanoparticles [107]. The enhanced dispersity of Pt nanoparticles will lead to a larger electrochemical surface area and higher electrocatalytic performance of Pt–S–C catalysts. As a result, many advanced *in situ* doping or post doping methods have been developed to synthesize SC as support for Pt catalysts.

Chen's group have developed a series of advanced SC supported Pt catalysts and investigated the effects of S doping in detail. Figure 6 shows a typical example of SC supported Pt catalysts from their group. In the study, S-doped graphene was synthesized by annealing graphene oxide together with phenyl disulfide as an S source, and Pt nanoparticles are homogeneously distributed on the SC support (Fig. 6(a)) [106]. The results of this investigation show that interactions between Pt and graphene are enhanced significantly by S doping (Fig. 6(b)), leading to a tethering effect and a downshift of the platinum d-band center and consequently enhanced stability of Pt (Fig. 6(c)). This method is effective for fabrication Pt, and Pt nanowires supported on S-doped graphene [107,108], Pt nanowires supported on S-doped CNTs [109] and PtNi nanoparticles supported on S-doped graphene [110] have been synthesized and shown to have enhanced activity and stability in electrocatalytic reactions. Fan et al. [111] developed a novel approach to synthesize S-doped CNTs as a support material for Pt nanoparticle catalysts. In the process, CNTs are annealed with poly(3,4-ethylenedioxythiophene) as the S source. Doping sulfur into the carbon support gives rise to a significant improvement in the dispersion of Pt and an increase in the electrochemically active surface area of the electrocatalyst.

3.4 Multiple doped carbon

As we mentioned above, the single heteroatom (N, B, S) doped carbon support can improve the electrochemical
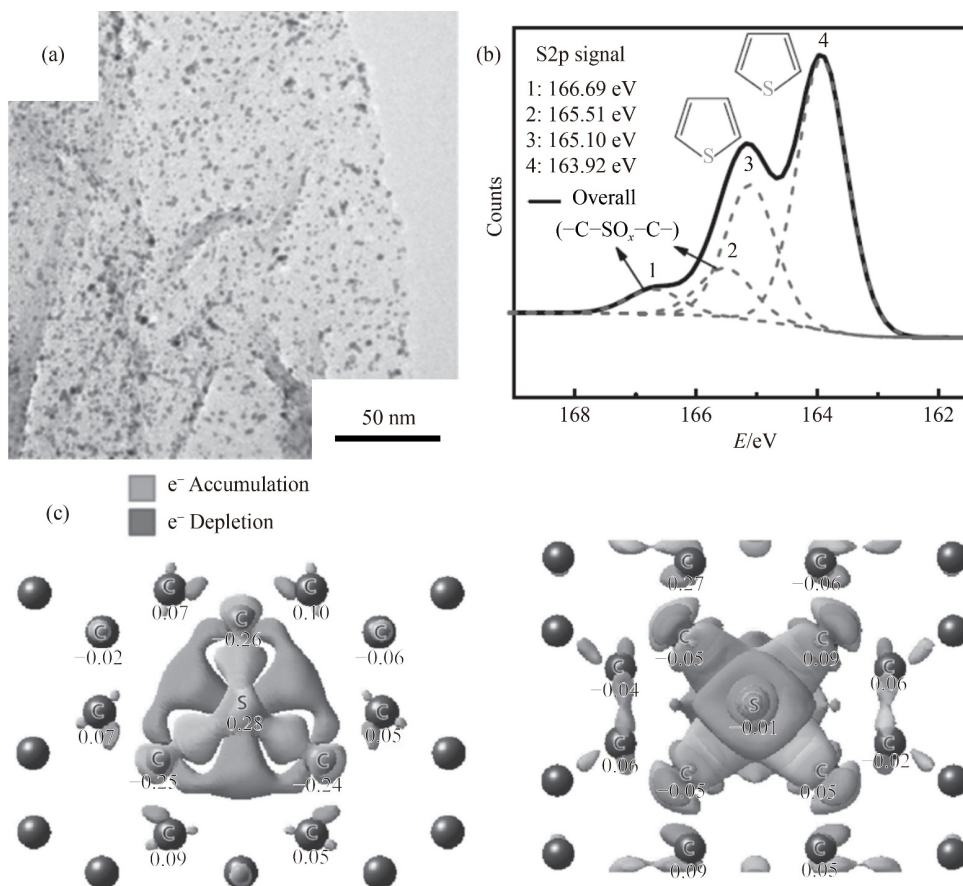
Fig. 6 (a) Morphology characterization, (b) S dopant characterization and (c) the electron structure characterization of Pt/SG. Reprinted with permission from Ref. [106], copyright 2014, Wiley-VCH.

properties of Pt catalysts to some extent. Multiple heteroatoms doped carbon, however, can further progressively enhance the electron transfer and thus the electrocatalytic performance owing to their different structures and bonding models [112]. Compared to the single-doped counterparts, multiple heteroatoms doping is more effective, because co-doped carbon supports can induce the formation of stronger active regions on the surface of carbon due to the synergistic effects of doping species [113]. Combining the strong electron acceptor effect of N, strong electron donor effect of B, and strong adsorbing nature of S, or other characteristics of heteroatoms such as F, P and Se, carbon supports which promote the rapid charge transfer and enhance the electrochemical activity of Pt catalysts were generated [114]. For example, the synergy of S and N together can significantly alter the spin electron density of C atoms adjacent to the heteroatoms, and thus greatly improve the electrochemical activity of multiple doped carbon supported Pt catalysts [115]. Moreover, the synergistic effect of triple doped carbon will prominently enhance the compatibility of material and electrolyte, endowing triple doped carbon supported Pt with higher kinetics of charge transfer and superior electrocatalytic performance [116]. As a result, the development of multiple doped carbon is highly

desired for high-performance design of carbon supported Pt-based catalysts.

Chang et al. [117] developed an effective method to synthesize N, S dual-doped mesoporous carbon involving annealing homemade acrylonitrile telomer as N and S sources. Owing to the dual-doping effects of N and S, Pt nanoparticles supported by this carbon material exhibit high catalytic activity and stability. Another facile method for fabrication of multiple doped carbon was developed by Zhu et al. [118]. In this effort, B, N dual-doped graphene sheets were synthesized by one-step pyrolysis of nitrogen and boron-containing borane-tert-butylamine complex. Using this material as a support for a Pt catalyst, promoted strong electron-donation to Pt and a created strong metal-support interaction, both of which highly facilitate the performance of the electrocatalyst.

4 Carbon-based binary support

Although carbon materials such as carbon black, graphene and CNTs are excellent supports for Pt-based catalysts, the weak nature of the chemical linkages often leads to a low structural stability and out-of-plane conductivity, which greatly limit their practical

applications [119,120]. Thus, hybrid carbon supports generated by utilizing a second support such as another carbon species, oxides or organics possessing different functions and effects is an advanced approach for materials design. Not only inheriting the advantages of the original support, materials created by addition another material to carbon could have synergetic effects that can be used to tune electronic structures, surface properties and functions of carbon supports. Thus, by using binary carbon-based materials as supports, Pt catalysts can be designed to have different properties and electrocatalytic performances.

4.1 Carbon/carbon

Several dual carbon/carbon composites, produced by combining carbon spheres, CNTs, CNF, graphene, carbon quantum dots (CQDs) and NC, have been developed as supports for Pt catalysts with increased conductivity and stability and improved performances. Our group has shown that a 3D nanocarbon hybrid support, composed of CNT and graphene, facilitates formation of sp^3-like defect structures, which leads to enhanced carrier transfer,

high structural stability and electrocatalytic durability [121]. Figure 7 shows some typical examples of carbon/carbon binary support supported Pt catalysts.

Using ultrathin zero-dimensional (0D) carbon to embed Pt is an advanced approach to developing high-performance electrocatalysts. A study by Ji et al. [122] led to the development of 0D/0D binary carbon composites to support Pt nanoparticles. In the fabrication process, Pt was supported on carbon black using a solvothermal method, and then high-temperature treatment was employed to transform an absorbed organic surfactant to a carbon shell, forming the Pt@C/C structure (Fig. 7(a)). Similarly, by using different carbon materials such as CNT or CNF as substrate followed by calcination of the organic compound on the Pt surface, 0D/1D (one-dimensional) binary carbon composites were prepared and assessed as supports in the Pt catalysts, forming Pt@C/CNT and Pt@C/CNF (Fig. 7(b)) [123,124]. In these catalytic systems, the carbon black substrates, CNT and CNF inherent their excellent properties, while the organic compound-derived carbon layer coating brings about better dispersion and protection from aggregation of the Pt nanoparticles, leading to the high activity and
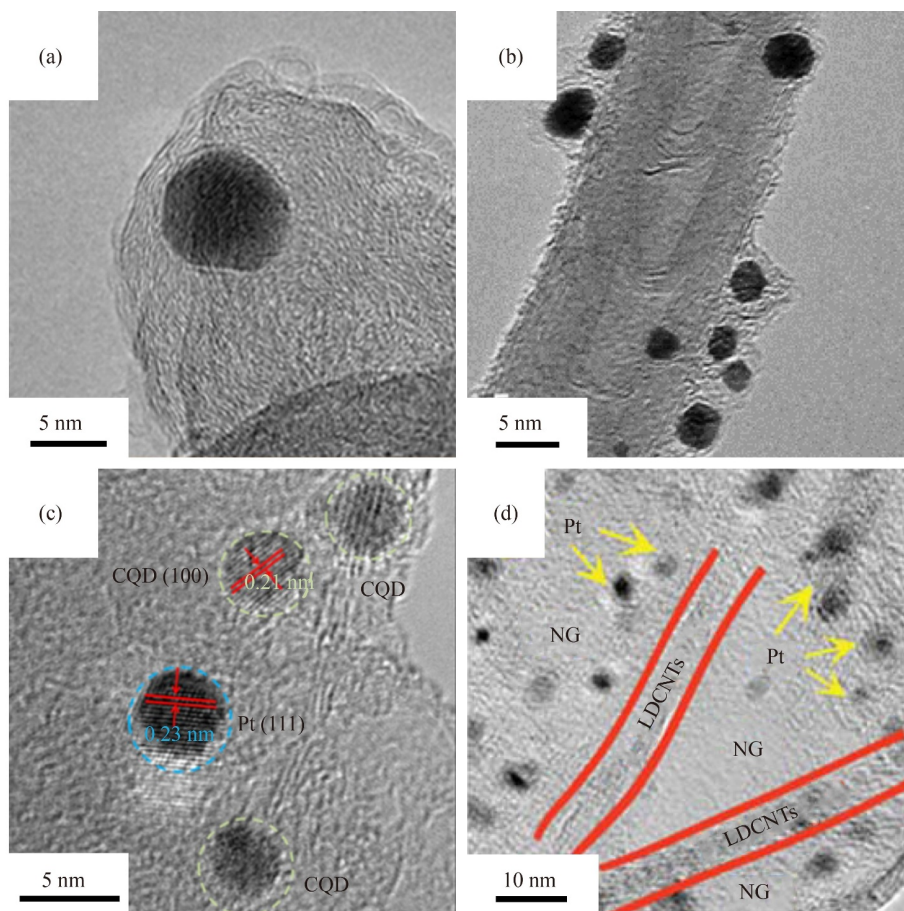

Fig. 7 Pt-based nanoparticles supported on (a) 0D/0D, (b) 0D/1D, (c) 0D/2D, and (d) 1D/2D carbon/carbon binary supports. Reprinted with permission from Ref. [122], copyright 2022, American Chemical Society, Ref. [123], copyright 2017, American Chemical Society, Ref. [127], copyright 2020, Elsevier, and Ref. [128], copyright 2018, American Chemical Society.

stability of electrocatalyst.

In addition to coated carbon, CQDs are another popular 0D carbon materials that have been utilized to composite other nanocarbons. Xiao et al. [125] combined CNT with composites of Pt nanoparticles and CQDs, and used the resulting material 0D/1D CQDs/CNT as a support for Pt. In a different way, Dang et al. [126] incorporated CQDs with carbon fiber cloths, then deposited Pt nanoparticles on the resulting 0D/1D carbon hybrids. In addition to these 0D/1D carbon hybrids, a 0D/2D (two-dimensional) CQDs/graphene support was developed by Xiao et al. [127] as a support for Pt (Fig. 7(c)). The CQDs with abundant anchoring points anchor Pt to gain high dispersity, while the combination of 0D CQDs with other carbon materials (1D CNT, 1D CNF or 2D graphene) greatly enhances the conductivity of carbon support. The synergy of 0D CQDs, substrate carbon and Pt leads to high performances of the supported Pt electrocatalyst.

Other kinds of carbon hybrids have been investigated. 1D/2D carbon aerogels composed of 1D CNT and 2D N-doped graphene were developed to support Pt by Yan et al. (Fig. 7(d)) [128]. The aerogel, having a low defect density, can effectively optimize the electronic structure and enhance the stability of Pt. Sun et al. [129] embedded Pt nanoparticles in a 1D@1D CNT@NC using a process in which Pt is anchored to the surface of CNT and the resulting complex is encased in organic material-derived NC. The formed sandwich structure endows Pt nanoparticle with minimal leaching, high protection and a modified electronic structure, which all lead to the high performance of catalyst.

4.2   Carbon/oxides

The use of nanostructured carbon materials has definitely led to enhancement of the performances of electrocatalysts by strong influencing both durability and electrochemical behavior. Unfortunately, carbon corrosion still occurs in these systems even though doping strategies have been developed to alleviate this problem. However, functionalization of the carbon support can make it more susceptible to electrochemical oxidation leading to loss of active surface area [130]. As a result, combining nanocarbons with other highly stable non-carbonaceous supports has become an important goal in studies designed to overcome the corrosion problem. Oxides are a type of inert supports that have received much attention. Studies have shown that strong metal support interactions occur in the oxides supported Pt-based system that strongly modify the electronic structure of Pt and, thus, enhance the performance of Pt based electrocatalysts [131,132]. Figure 8 shows some typical examples of carbon/oxides binary support supported Pt catalysts.

SiO$_2$, well known for its hardness and existence in a variety of crystalline as well as amorphous states, was initially used as an essential component of self-

humidifying membranes in fuel cells. Recently, SiO$_2$ and carbon have been utilized as binary support materials for Pt electrocatalysts. In an effort by Park et al. [133], a SiO$_2$/C binary support for Pt was formed by coating commercial Pt/C catalysts with SiO$_2$ shells using a hydrolysis reaction of a SiO$_2$ precursor. Introduction of SiO$_2$ into the support effectively enhances proton conductivity as well as the performance of catalyst. Similarly, Islam et al. [134] coated carbon black with SiO$_2$ shell by employing the same hydrolysis reaction, and then used the material as a support for Pt (Fig. 8(a)). The results of this study show the protective shell created using SiO$_2$ coating prevents carbon corrosion and platinum dissolution.

TiO$_2$ materials have been widely used as conductive oxides due to their excellent corrosion resistance in various electrolyte media. These oxides have good photoelectrochemical as well as electrocatalytic properties. Barbosa et al. [135] investigated the effect of using TiO$_2$ as a co-support. In the fabrication process, Pt nanoparticles were first deposited on the surface of TiO$_2$, and the formed Pt/TiO$_2$ was then supported on carbon black to form Pt/TiO$_2$/C composites. TiO$_2$ engages in metal-support interactions which enhance catalytic activities via the generation and exposure of surface-active sites with improved stabilities. Lee et al. [136] fabricated the two electrocatalysts, Pt/TiO$_2$/C and TiO$_2$/Pt/C, by introducing respective TiO$_2$ layers or coatings during the *in situ*-synthesis of the Pt/C catalyst (Fig. 8(b)). Both catalysts exhibit higher durability than the native Pt/C catalyst, and TiO$_2$/Pt/C with a TiO$_2$ layer coating on the Pt surface has a better initial performance, indicating the introduction of TiO$_2$ as co-support enhances both activity and stability of Pt catalysts.

Iron-, cobalt- and nickel-based oxides containing supports have also attracted much attention owing to their inherently high electrocatalytic performance. For example, de Oliveira et al. [137] found that composites of nano nickel oxides (NiO$_x$) with commercial Pt/C catalyst (Fig. 8(c)) facilitate oxidation of adsorbed H atoms by the OH species at Ni sites on the Pt surface, which leads to high electrocatalytic performance. Gu et al. [138] fabricated a cobalt oxide (Co$_3$O$_4$)/NC matrix by using direct pyrolysis of cobalt-based precursors on supported Pt nanoparticles. The composite support forms a strong metal-support electronic interaction, which facilitates dispersion of Pt nanoparticles and oxidative cleavage of O–H bonds.

In addition to the oxides described above, many others have been investigated as co-supports in catalysts. For example, Song et al. [139] found that deposition of TaO$_x$ nanoparticles on the Pt surface of the commercial Pt/C catalyst leads to formation of a triple-junction structure (Fig. 8(d)), which anchors TaO$_x$ via strong metal oxide-support interactions, and it therefor enhances the stability of Pt-based catalyst. Ma et al. [140] developed a delicate
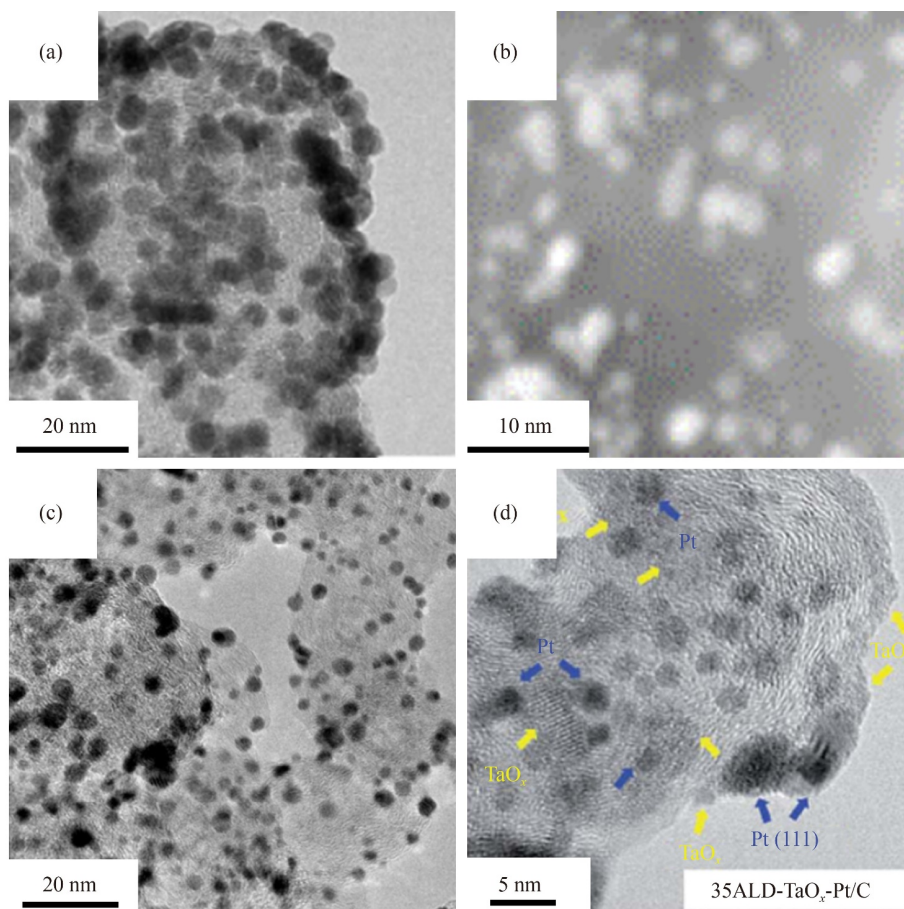
Fig. 8 Pt-based nanoparticles supported on (a) carbon/SiO$_2$, (b) carbon/TiO$_2$, (c) carbon/NiO$_x$, and (d) carbon/TaO$_x$ binary supports. Reprinted with permission from Ref. [134], copyright 2021, Elsevier, Ref. [136], copyright 2022, American Chemical Society, Ref. [137], copyright 2017, Elsevier, and Ref. [139], copyright 2017, American Chemical Society.

approach that involves first embedding NbO$_x$ in pores of nanoporous carbon, and then depositing Pt nanoparticles on the top of NbO$_x$ to form catalyst Pt/NbO$_x$/C. The co-support NbO$_x$ creates strong metal-support interactions that maximize Pt utilization, minimize particle agglomeration, carbon corrosion and metal oxidation, and enhance electrocatalytic performance.

4.3   Carbon/organics

Organics with low conductivity are not suitable as support or co-support materials in electrocatalysts. However, many conducting polymers, including polypyrrole, polyindole, poly(3,4-ethylenedioxythiophene), polyaniline and poly(diallyldimethylammonium chloride) have been shown to be promising co-supports. As binary supports with carbon species, these organics bring about a number of different effects. Figure 9 shows some typical examples of carbon/organics binary support supported Pt catalysts

He et al. [141] developed a polyaniline/CNT binary support for Pt catalysts. In the support, polyaniline is attached to CNT through π–π interactions of aniline moieties and the conjugated π system on the CNT surface (Fig. 9(a)). This interaction in the support prevents Pt aggregation owing to aniline protection. As well, the co-support forms a strong covalent bond with Pt, which leads to high dispersion and electrocatalytic performance of Pt nanoparticles. Fan and Sun's group [142] prepared a series of polymer/carbon supported Pt catalysts by first using poly(3,4-ethylenedioxythiophene) and MnO$_x$ to form a composition material with CNT to support Pt nanoparticles. A binary support composed of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(p-toluenesulfonate) with graphene was generated (Fig. 9(b)) [143]. This polymer/carbon support has high proton conductivity, and it enhances the dispersion, electrocatalytic activity and stability of Pt nanoparticles. This group also created a composite of CNT and polyindole for use as a support for Pt (Fig. 9(c)) [144]. The N-containing polyindole engages in a strong Pt−N interaction, which further improves the electrocatalytic performance of the Pt catalyst.

In addition to conducting polymers, MOFs also have shown to have a high potential as co-supports with carbon. Eßbach et al. [145] found that mixing Pt/carbon
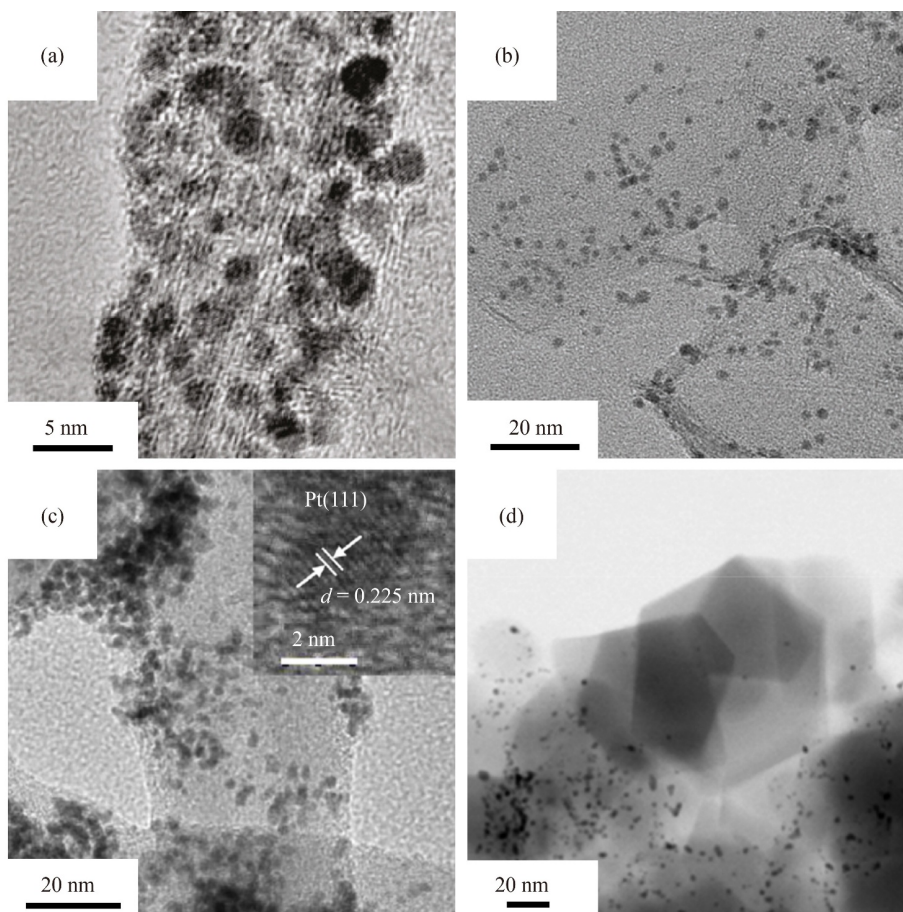
Fig. 9 Pt-based nanoparticles supported on (a) carbon/polyaniline, (b) carbon/5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate), (c) carbon/polyindole, and (d) carbon/ZIF-8 binary supports. Reprinted with permission from Ref. [141], copyright 2011, American Chemical Society, Ref. [143], copyright 2014, Royal Society of Chemistry, Ref. [144], copyright 2015, Elsevier, and Ref. [145], copyright 2019, American Chemical Society.

black catalyst with ZIF-8 precursors leads to facilitation of the growth of ZIF-8 nanoparticles on Pt/C (Fig. 9(d)). It was shown that addition of ZIF-8 gives the Pt/C catalyst a high selectivity for electrooxidation of small alcohols.

5   Electrocatalytic applications of carbon-supported Pt-based catalysts

In the previous sections, we discussed the Pt–C interactions brought by using various carbon-based supports that enable effective tuning of the physiochemical properties and electronic structure of Pt. In this section, we will briefly discuss some application of these novel carbon-supported Pt-based catalysts to specific electrocatalytic reactions, as shown in Fig. 10.

The ORR occurs at the cathode of proton exchange membrane fuel cells. Because the properties of the ORR electrocatalysts govern the overall performance and efficiency of these fuel cells, large efforts have been dedicated to improving both the activity and stability of

carbon supported Pt catalysts. Carbon materials themselves can serve as the catalysts for ORR, especially those heteroatoms doped or well-functionalized ones which have abundant active sites on the carbon surface [89]. When used as support for Pt catalysts, carbon materials will stabilize Pt nanoparticles to enhance their dispersity, encapsulate Pt to prevent from aggregation, or form a synergistic effect with Pt to co-catalyze ORR. For example, Choi et al. [146] prepared a high-performance catalyst by using cross-linkable block copolymer-based carbon as a support in Pt-based catalyst having an ultralow Pt loading. Embedding of PtFe nanoparticles in the porous carbon shell provides this catalyst with higher durability than commercial Pt/C, as is reflected in the observation that only 1/20 of the Pt is consumed after 30000 potential sweep cycles. The high-performance could be ascribed to the large surface areas of the mesoporous carbon support facilitating reactant adsorption and mass transport, the porous structure of carbon encapsulating the PtFe nanoparticles and preventing them from oxidation and aggregation, and the small particle size of PtFe catalyst. Our group demonstrated that using a highly graphitic CNF carbon support for bimetallic PtPd
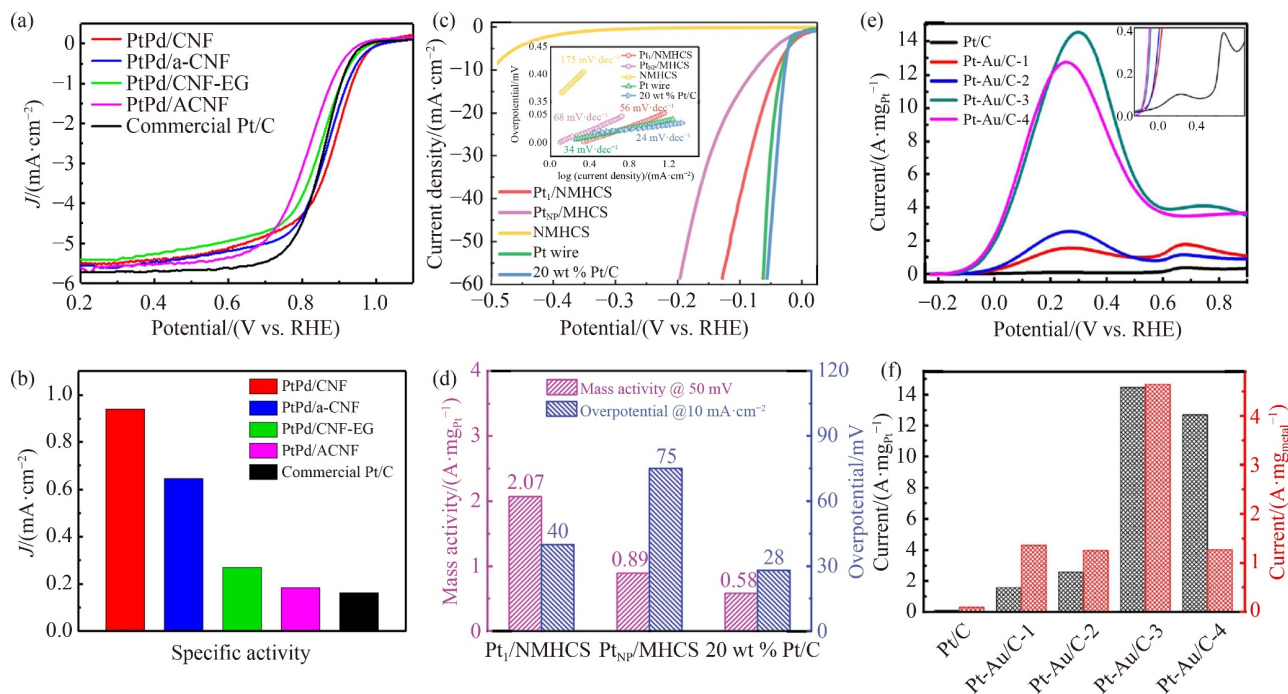
Fig. 10 (a) ORR polarization curves and (b) corresponding specific activities of PtPd/CNF, PtPd/a-CNF, PtPd/CNF-EG, PtPd/ACNF, and commercial Pt/C. Reprinted with permission from Ref. [147], copyright 2019, Elsevier. (c) HER polarization curves of Pt_1/NMHCS, PtNP/MHCS, NMHCS, Pt wire and 20 wt % Pt/C. (d) Corresponding mass activities and overpotential of Pt_1/NMHCS, PtNP/MHCS and 20 wt % Pt/C. Reprinted with permission from Ref. [111], copyright 2019, Wiley-VCH. (e) FAOR cyclic voltammetry curves and (f) corresponding mass activities of Pt-Au/C and Pt/C. Reprinted with permission from Ref. [113], copyright 2018, Elsevier.

nanoparticles creates the PtPd/CNF catalyst, which exhibits a 5.8 fold higher ORR activity than commercial Pt/C (Figs. 10(a) and 10(b)) and a high stability over 8000 potential sweep cycles [147]. The high ORR performance of this catalyst is attributed to the presence of sp^2 bonded graphitic CNF, which cause a low level of defects, and participates d−π effects between CNF and Pt that greatly modifies the Pt 5d orbital energies.

The HER takes place at the cathode in electrocatalytic water splitting. Although Pt-based materials are the most efficient catalysts for this process, their low activities and low stability under alkaline conditions remain as key obstacles that need to be addressed [148]. Carbon materials are seldom directly active toward HER. Thus, as support for Pt, their main functions are to modify the electron structure of Pt for better hydrogen adsorption feature or to stabilize Pt nanoparticles. The N-doped hollow carbon sphere in supports developed by Kuang et al. [73] engage in strong electronic interactions with Pt. These materials exhibit a high performance toward the HER, associated with a low overpotential of 40 mV at a current density of 10 mA·cm^{-2}, a high mass activity of 2.07 A·mg^{-1} Pt at 50 mV overpotential, a large turnover frequency of 20.18 s^{-1} at 300 mV overpotential, and outstanding durability (Figs. 10(c) and 10(d)). By confining sub-nanometer Pt clusters in hollow mesoporous carbon spheres, the catalyst developed by Wan et al. [72] has a 12 times higher mass activity than that of a similar

loading of Pt in commercial Pt/C catalyst. The high HER performance is ascribed to the strong interaction between the carbon support and Pt catalysts as well as the hollow porous sphere morphology which provides effective protection and efficient mass transfer.

Electrocatalysis of small organic molecules is an important application of carbon supported catalysts. Despite the co-catalytic active sites, electron structure tunning effect and stabilization functions, the porous structure of carbon may be of vital significance owing to the bigger molecular size of these organics compared to hydrogen or oxygen. Thus, highly porous materials with specific surface area for high availability of reactant on Pt surface are highly desired. Bai et al. [149] showed that a catalyst comprised of uniformly deposited and well-distributed Pt nanoparticles on an atomic carbon layer has a higher catalytic activity in methanol oxidation reaction with a 647.63 mA·mg^{-1} at a peak potential of 0.85 V and much improved anti-CO poisoning ability than that of commercial Pt/C, Pt/CNTs and Pt/graphene catalysts. The high specific surface areas and improved conductivities brought by the presence of the atomic carbon layer make Pt highly active for methanol oxidation. By fabricating a trijunction of Pt, CQDs and CNT, Perini et al. [88] created a catalyst that has a mass activity of 4917 mA·mg^{-1} Pt in ethanol oxidation reaction, which is 5.6 times higher than that of commercial Pt/C. The synergy between CQDs and CNT greatly

improves the catalytic performance of Pt not only because of the abundant anchoring points of CQDs for fixation and dispersion of Pt, but also the 3D conductive network of CNT/CQDs to enhance the conductivity of materials [150]. Fan et al. [151] devised a catalyst in which Pt and Au are uniformly distributed on carbon black using an ultrasound-assisted method in the absence of a surfactant. The catalyst has a high performance toward the formic acid oxidation reaction (FAOR) associated with a remarkable 153 times higher mass activity than that of commercial Pt/C (Figs. 10(e) and 10(f)). The high dispersity of Pt and Au nanoparticles on carbon black play a key role in determining the high catalytic performance of this catalyst.

6   Summary and outlook

In this review, we provide an overview of recent developments made in studies of carbon-supported Pt-based electrocatalysts with special attention being given to effects on and of Pt–C interactions. Impacts of the supports on the growth, particle size, morphology, dispersion, electronic structure, physiochemical properties and functions to Pt catalysts are discussed. The design of high-performance Pt-based electrocatalysts comprised of novel carbon supports, including porous carbon, heteroatom doped carbon and carbon-based binary systems, are summarized, and applications of these materials in electrocatalysis are presented. With major goal being the attainment of improved catalytic performance, these efforts have concentrated on the development of supports that give the catalysts high stabilities, and that facilitate dispersion of Pt nanoparticles, tune Pt electron structures and increase interaction with Pt. The results of these efforts show that using supports comprised of large surface area and highly porous carbon materials, such as OMC, MOFs-derived porous carbon and 3D porous carbon, to encapsulate nanosized Pt materials greatly facilitates anchoring and dispersion of Pt nanoparticles, which leads to exposure of greater numbers of active sites and protection of Pt from corrosion or poisoning, both of which result in improvements in the activity and stability of Pt catalyst. Doping carbon materials with N, B, S or multiple atoms with different electron donor and/or acceptor features results in carbon supports that engage in strong metal-support interaction, and even form bonds with Pt, which govern the electron structure of Pt, thus lead to the high electrocatalytic performance. Furthermore, compositing carbon materials with another carbon, oxide or organic material give rise to binary supports that combine beneficial functions of the two materials, form 3D composite junctions and provide effective protection to carbon supported Pt catalyst.

Based on the issues examined in this review, we have a list of several important future research directions, listed below, that could be followed in future studies aimed at understanding relationships that exist between Pt–C interactions and performances of Pt-based electrocatalysts and developing highly active and durable carbon-supported materials for this purpose.

(1) Choose reasonable carbon support for catalysts that promote specific electrochemical reactions. The results of the studies reviewed above show that by considering morphologies, sizes, porous features and functions, in the future it should be possible to design carbon materials that promote high dispersion of the metal, high resistance to corrosion and poisoning, and optimal mass and electron transfer that are required to obtain optimal catalytic efficiencies for specific electrochemical reactions.

(2) Obtain optimal Pt–C interactions. Although many reports indicate that high catalytic performances can be obtained by strengthening metal-support interaction, especially in the heteroatom doped carbon and binary carbon supports, it is worth noting that unguided searches for systems that have strong Pt–C interactions could lead instead to decreased catalytic performances. Accordingly, strong metal-support interactions could also block the active sites already present in Pt, or cause strong absorption of substances on the Pt surface, resulting in lower absorbance and/or desorption of reactants. Therefore, rational designs of optimal Pt–C interactions in carbon supported Pt catalysts are needed.

(3) Develop multiply functional catalysts. By properly tuning the physiochemical properties and electronic structures of carbon, it should be possible to create carbon materials that are endowed with new functions. Moreover, the indigenously high activities of Pt Catalysts formed by using heteroatom doped carbon materials as supports are expected to increase when composites of carbon and other active materials are employed. It is anticipated that combining the beneficial characteristics of both materials, the supports will give catalyst multiple functions and high efficiencies.

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